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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C23C 14/22	A1	(11) International Publication Number: WO 96/32520 (43) International Publication Date: 17 October 1996 (17.10.96)

(21) International Application Number: PCT/US96/05101

(22) International Filing Date: 12 April 1996 (12.04.96)

(30) Priority Data:
08/423,645 14 April 1995 (14.04.95) US

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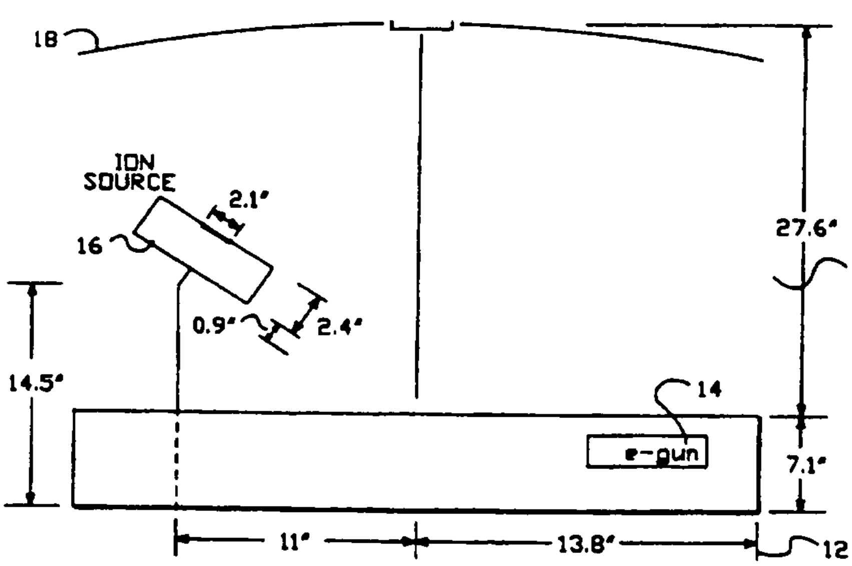
(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: METHOD FOR PRODUCING DIELECTRIC COATINGS



(57) Abstract

A method for creating a dielectric coating on a substrate produces near bulk density metal oxide coatings with extremely low surface roughness, microstructure and low defect density. The coatings have a low scatter of less than 50 ppm, low loss of less than 100 ppm, and an environmental stability of 0.1 or less spectral shift. A high vacuum chamber is provided which includes a substrate carrier device (18), an electron beam gun (14), a substrate, an evaporant source of coating material (12), a plasma bridge neutralizer (not shown) and an ion gun (16). Coating material is evaporated with the electron beam gun to form a coating material evaporant that is directed to the substrate. An ion gun is directed toward the substrate and produces ions that arrive substantially simultaneously with the coating material evaporant at the substrate. The ions provide a momentum assist to the coating material. The result is a formation of a desirable dielectric thin film of coating material on the substrate.

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METHOD FOR PRODUCING DIELECTRIC COATINGS

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates generally to the formation of dielectric thin films on a substrate, and more particularly to a method for producing thin films on a substrate utilizing an electron beam gun to create evaporated coating molecules that are deposited on a selected substrate, an ion source, and a plasma neutralizer, wherein ions and evaporated coating material arrive substantially at the same time at the substrate, forming a low scatter, low loss, near bulk density dielectric thin film coating with relatively low surface roughness, and a microstructure with low defect density.

Description of the Related Art

The traditional method of fabricating dielectric thin films on selected substrates have been the utilization of an electron beam evaporation method. Such a method utilizes a substrate on which a thin layer coating is applied, with the substrate positioned inside of a vacuum chamber, along with a sample of the bulk or target material that is deposited. An electron beam focussed on the sample material causes localized heating of the material to a point where molecules are evaporated off. These molecules then condense on the other surfaces located in the interior of the vacuum chamber, including the substrate which is being coated.

An electron beam has been utilized because of its capability of transferring sufficient thermal energy to a localized area of the target material. The kinetic energy of the electrons in the beam are converted to thermal energy when the beam is directed at the evaporate material. Molecules of the target material are heated to the point where molecules or grouped molecules are boiled off. This process of electron beam evaporation as a method of coating is

thoroughly explained in, "Physical Vapor Deposition," distributed by Airco Temescal, 2850 Seventh Street, Berkeley, California, 1976.

One of the principle problems encountered in the electron beam evaporation technique is to coat layers so they approach the density of the bulk material from which they come. With this process, molecules of the target material condense on the substrate in such a manner that voids, pores and holes are left between them. The resulting coating is less dense than the bulk, which results in a difference in the layers index of a refraction. Because of the unpredictability of the final density, it is difficult to determine and to control the refractive indexes of the stack.

Another problem with the electron beam technique is encountering impurities or air pockets in the target material. The high heat concentration results in small explosions which throw larger chunks of coating materials throughout the chamber that represent impurities which condense in the layer. These impurities increase point or defect scatter and absorption.

With the electron beam evaporation technique, parameters including temperature of the substrate, partial pressure of oxygen in the chamber, rate of deposition, and preparation of the target material are varied attempts to control and improve the oxidation state, packing density, and degree of amorphousness of the layers. Generally, determining the proper variations and controlling them has proven difficult. Typically, the temperature of the substrate must be maintained at about 300 degrees centigrade. However, the energy of the electron beam evaporant is about 0.1 eV, and high packing density of the coating material on the substrate is not achieved.

More recently, a method for fabricating multilayer optical films has been reported in U.S. Reissue Number 32,849. In the '849 patent, an ion gun is utilized and directed to strike target material. The energy of the ion gun is about 500-1000 eV, and the energy of the evaporant is about 10 eV. The result is dielectric thin film formation with low scatter, low loss, and dense films. However, the system for achieving this result is relatively expensive. Further,

this method requires critical alignment and geometry which can be difficult to achieve.

Accordingly, there is a need to achieve a method for creating dielectric thin films on substrates with low scatter, low loss, and dense films that is economically suitable for retrofitting existing systems. Further, there is a need for such a method to which an electron beam gun produces evaporant coating material that encounters ions which transfer momentum to the coating material substantially on the substrate.

SUMMARY OF THE INVENTION

Accordingly, the present invention provides a method for forming dielectric thin films on substrates that have low scatter.

Another object of the invention is to provide a method for forming dielectric thin films on a substrate with low loss.

Yet another object of the invention is to provide a method for forming dielectric thin films on a substrate with a spectral shift of 0.1 percent or less.

A further object of the invention is to provide a method for forming dielectric thin films on a substrate that are highly dense, near bulk value, and a microstructure that has minimal voids or holes.

Still a further object of the invention is to provide a method for forming dielectric thin films on a substrate which are environmentally stable.

Yet another object of the invention is to provide for forming dielectric thin films on a substrate while maintaining extremely low surface roughness values over a large number of layers, and over a range of layers thicknesses.

Another object of the present invention is to provide a method for forming dielectric thin films on a substrate that are highly efficient oxygenation of a metal oxide dielectric thin film deposition.

A further object of the invention is to provide a method for forming dielectric thin films on a substrate that employs a plasma bridge neutralizer.

Still a further object of the invention is to provide a method for forming dielectric thin films on a substrate at a slow rate of deposition to allow a desired

arrival rate of ions and evaporant coating substantially simultaneously at the substrate surface.

Another object of the invention is to provide a method for forming dielectric thin films on a substrate with a maintainable arrival rate of ions and evaporant coating material.

Yet another object of the invention is to provide a method for forming dielectric thin films on a substrate which utilizes a momentum transfer from oxygen ions to the evaporant coating material.

These and other objects of the invention are achieved in a method for creating an dielectric coating on a substrate. The method provides a high pressure vacuum chamber including a substrate carrier device, an electron beam gun, a substrate, and an evaporant source of coating material, a plasma neutralizer and an ion gun. Coating material is evaporated with the electron beam gun and forms a coating material evaporant that is directed towards the substrate positioned on the substrate carrier. The ion gun is directed toward the substrate and produces ions that arrive substantially simultaneously with the coating material evaporant at the substrate surface. The ions provide a momentum assist to the coating material. A dielectric thin film coating is then formed on the substrate.

In another embodiment, the method provides a high vacuum chamber including a substrate carrier device, an electron beam gun, a substrate, an evaporant source of coating material, a plasma beam neutralizer and an ion gun producing positively charged particles along a longitudinal axis of the ion gun. The plasma beam neutralizer is positioned adjacent to and in a lateral direction relative to the ion gun longitudinal axis. Electrons are generated from the plasma beam neutralizer which mix with the positively charged particles along the longitudinal axis of the ion gun at the exterior of the ion gun, producing a beam of flowing plasma. Coating material in the electron beam gun is evaporated and forms a coating material evaporant that is directed to the substrate. The beam of flowing plasma provides a momentum assist to the

coating material evaporate. A dielectric thin film of coating material is then formed on the substrate.

A plurality of dielectric thin films of the coating material are formed on the substrate. The stoichiometry of the coating material layers formed on the substrate are controlled. The ion/coating material evaporant arrival ratio at the substrate is controlled to create a desired density of coating material dielectric thin film layers. Further, the ions are utilized in order to increase the energy of the coating material deposited as layers on the substrate.

In one embodiment of the invention, the energy of the coating material deposited as layers on the substrate is greater than five eV, preferably greater than 7.5 eV, still more preferably greater than 9.0 eV, and still more preferably, 10.0 eV or greater.

The electron beam gun provides the evaporant flux which is deposited on substrates positioned in the carrier. A uniform flux is applied substantially under a carrier of a high vacuum evaporant chamber. The dielectric thin film coatings have low scatter of about less than 50 ppm, low loss of about less than 100 ppm, and a spectral shift of 0.1 percent or less.

The method of the present invention provides high energy coating molecules at the substrate level. For example, when the coating is metal oxide, the present invention provides near "fluid motion" for the evaporated molecules during film formation. The initial fluid motion of monolayers, however, does not continue for a very long time since the substrate acts as a heat sink and causes the molecules to freeze in place. In this energetic fluid motion process, filling of voids occurs in microstructures and coating surfaces are smooth.

With the present invention, an electron beam gun is utilized to evaporate metal oxide, metal fluroide, metal carbide and metal nitride targets including but not limited to tantala, zirconia, hafnia, titania and silica of varying oxidation states. The evaporated target molecules subsequently condense and coalesce on a preheated, approximately 200 degrees centigrade, substrate surface. At the initial stages of evaporation, e.g., at the target level, the energy of the coating molecules is approximately 0.1 eV. However, at the substrate level, the energy

of the coating vapor is boosted to about 10 eV. This energy is transferred or imparted to the coating molecules via a collisional process with energetic oxygen ions, of specified energy and flux, at the substrate level where the dielectric thin film microstructures take form. In this method, a key parameter is the ion/evaporant molecule arrival ratio which determines the density of the growing film.

The present invention further provides for ion beam neutralization. This is also referred to as space/charge neutralization. In space/charge neutralization, free electrons are allowed to mix with molecular ions without being captured by the electronic shell of the ions. Thus, the injection of free electrons into the ion beam in essence produces a beam of flowing plasma.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a cross-sectional view of the high vacuum chamber utilized with the method of the present invention.

Figure 2 is a cross-sectional view of the electron beam gun utilized with the method of the present invention, including relative dimensions.

Figure 3 is an illustration of the ion source inclination angle.

Figure 4 is a cross-sectional downward view from the top of the high vacuum chamber in the present invention.

Figure 5 is a table of the refractive index as a function of deposition rate for Ta_2O_5.

Figure 6 is a table of the refractive index as a function of deposition rate table for TiO_2.

Figure 7 is a schematic drawing of an ion source suitable for use with the method of the present invention.

Figure 8 is a schematic diagram of an anode ring used in the ion source of the present invention.

Figure 9 is a schematic diagram of the ion source in the neutralizer suitable for use with the present invention.

Figure 10 is a schematic diagram of the neutralizer.

Figure 11 is a perspective view of the cold cathode plasma bridge neutralizer of the present invention.

Figure 12 illustrates the relative position of the plasma bridge source in the cold cathode ion source.

Figure 13 is a schematic diagram illustrating the vacuum chamber with oxygen and argon gas feeds.

DETAILED DESCRIPTION

The present invention provides a method for creating an dielectric coating on a selected substrate within a high vacuum chamber. A high vacuum chamber is utilized and includes a substrate carrier, an electron beam gun, a substrate positioned in one of the carrier elements, an evaporant source of coating material that serves to create the thin layers on a substrate, a plasma beam neutralizer and an ion gun. The coating material is evaporated with the electron beam gun and forms a coating material evaporant that is directed towards the carrier, and more particularly, to the individual substrates in the carrier. The ion gun is also directed toward the substrate and produces ions that arrive substantially simultaneously with the coating material evaporant at the substrate. The ions provide a momentum assist to the coating material. Finally, a dielectric thin film, such as a multilayer stack, of various thicknesses, is then formed on the substrate.

Further, the method provides a high vacuum chamber including, a substrate carrier device, an electron beam gun, a substrate, an evaporant source of coating material, a plasma beam neutralizer and an ion gun producing positively charged particles along a longitudinal axis of the ion gun. The plasma beam neutralizer is positioned adjacent to and in a lateral direction relative to the ion gun longitudinal axis. Electrons are generated from the plasma beam neutralizer which are mixed with the positively charged particles. Multiple layers can be formed, including but not limited to layers of different materials, i.e., alternating layers. More than 50 layers can be formed. The dielectric coating has a low surface roughness of less than 5 Å RMS when

deposited on a substrate of less than 2 Å RMS. Further, the dielectric coating is near bulk density or bulk density which means 0.95 or greater. It will be appreciated that the dielectric coating can be a optical coating.

Referring now to Figures 1-4, a vacuum chamber 10 is provided. Disposed within vacuum chamber 10 is a base plate, 12, in which an electron beam gun, 14, is positioned. In one embodiment of the invention, the electron beam gun has an crucible pocket of about 1.75 inches in width, it is positioned above base plate 12, 5 1/8 inches, and is approximately 1/2 inches in depth. The crucible pocket houses the evaporant coating material. Suitable coating materials include metal oxides, metal fluorides, metal carbides and metal nitrides. Exemplary coating materials include but are not limited to SiO_2, HfO_2, Ta_2O_5, ZrO_2, TiO_2, SiO_2, HfO_2, Ta_2O_5, ZrO_2, TiO_2, , Nb_2O_5, Y_2O_3, Al_2O_3, Se_2O_3, BeO, Gd_2O, AlF_3, MgF_2, ThF_4, HfF_4, YbF_3 and YF_3. Evaporated target molecules are caused to condense and coalesce on a preheated, 200 degree Centigrade, substrate surface. At the initial stages of evaporation, e.g., at the target level, the energy of the coating molecules is approximately 0.1 eV. At the substrate level the energy of the coating vapor is boosted to 5 eV or greater, preferably 7.5 or greater, still more preferably 9.0 or greater, and most preferably about 10 eV. This energy is transferred or imparted to the coating molecules via a collisional process with energetic oxygen ions, of specific energy and flux, on the substrate where the dielectric thin film microstructures take form. A key parameter for this process is the ion/evaporant molecule arrival ratio which determines the density of the going film, as illustrated in Figures 5 and 6, for Ta_2O_5, and TiO_2, respectively.

In the case of Ta_2O_5, a time period for deposition was 3 minutes, 10 minutes, and 25 minutes. The evaporant flux was 4.4×10^{14} molecules per s cm^2, 1.3×10^4 molecules/s cm^2 and 4.9×10^{13} molecules/s cm^2, respectfully; the ion flux at 3 minutes was zero ions, at 10 minutes it was 5.4×10^{14} molecules/s cm^2, and at 25 minutes, 5.4×10^{14} molecules/s cm^2. The evaporation:ion ratio at 10 minutes was 1:4.2, and at 25 minutes 1:1.1. Refractive indexes were measured at 3 minutes at 2.05, 2.12 at 10 minutes, and

2.20 at 25 minutes. The coating temperature was at 200 degrees C, the ions species was oxygen and the ion energy was approximately 550 eV, e.g., the plasma energy inside of the ion source. Figure 6 has similar data for TiO_2. Again, this emphasizes the significance of the rate of ion:evaporant molecule arrival ratio. The proper ratio is required in order to achieve a highly dense, nearly bulk value, and microstructure with the concaminont effect being very high and an environmentally stable refractive index. The coatings deposited maintain extremely low surface roughness values over a large number of layers, and over a range of layer thicknesses. Additional characteristics include the high efficient oxygenation of the metal oxide dielectric thin film during deposition. This is a consequence of the high oxygen ion:evaporant molecule arrival ratio from the coating process. Further, a very good adhesion of the coating is achieved on the substrate. These features combine with the method's inherent generation of low defect density, yields dielectric coatings with total losses of less than 100 ppm at 633 nm, as coated on superpolished substrates of less than 1 Å RMS. Near bulk density metal oxide coatings with low scatter, less than 50 ppm, low loss, less than 100 ppm, environmentally stable, less than 0.1 percent spectral shift, are achieved.

Referring again to Figures 1-4, a specific embodiment of the invention is disclosed. As shown in Figure 1, selected dimensions are suggested, but those skilled in the art will appreciate that the present invention is not limited to the dimensions stated in Figure 1. As shown in Figure 1, electron beam gun 14 is positioned in base plate 12 within vacuum chamber 10. Ion source 16 is positioned closer to dome 18 of vacuum chamber 10. A carrier 20 is positioned adjacent to dome 18, and includes a plurality of carrier elements to hold and maintain a plurality of substrates to be coated. As shown in Figure 2, dimensions of the electron beam gun 14 are illustrated. In Figure 3, a 21 degree ion source inclination angle is shown. Ion source 16 is tilted in order to achieve the proper coverage for the substrates. Further, in Figure 4 a monitor window, 22, permits viewing and monitoring of the process. A specific embodiment is illustrated in Figure 4 wherein the center of electron beam gun crucible 14 is

illustrated relative to the center of ion source 16. The point of intersection of the ions and evaporant is at a point 24. One will appreciated that the point of interaction between the ions and coating molecule evaporant is at the substrate level. The interaction of the two does not occur prior to interaction at the substrate level in order to maintain the desired momentum transfer. Therefore, it is important to maintain the total chamber pressure to about 1.0 X 10_{-4} during deposition.

Referring now to Figure 7, ion source 16 includes an oxygen flow channel 26 which introduces oxygen within an interior of ion source 16. Ion source 16 includes an anode ring 28 which is connected to a current source that is regulated. In one embodiment of invention, 400 mA are delivered to anode ring 28.

For purposes of the present invention, an ion neutralizer 30 is associated with ion source 16. The oxygen ion beam utilized to impart energy to the growing dielectric thin film is generated and extracted from a cold cathode ion source such as model cc-102r, available from Danton Vacuum. Oxygen ions are generated when neutral oxygen gas is injected into a region of strong static electric field. In the region of strong electric field, outermost electrons are stripped from neutral diatomic oxygen producing ionized monatomic and diatomic oxygen. This region consists of neutrals, ions and electrons, generally referred to as a glow discharge or plasma, and immersed in a strong, static magnetic field of about 3000 Gauss. The magnetic field serves the purpose of creating a helical-type motion path for the electrons. This increases its collisional cross-section with neutral oxygen gas. Ion source 16 voltage utilized for plasma generation can be about 550 volts +/- 10 percent, at an oxygen injection rate of about 12 sccm (or calibrated chamber pressure of approximately 7.0 x 10^{-5} torr(GP)). In ion source 16, the voltage, or indirectly the electric field, is maintained between an anode and a cathode with circuitry configured for current limited mode, with the cathode at ground potential. Due to the cathode being at ground potential, the anode voltage with respect to ground defines the plasma potentials for the ion energy. In the ion extraction

process, the ions inside ion source 16 float at a plasma potential typically about +10 volts above the anode voltage. These positive ions subsequently accelerate down the "potential hill" as they are pulled by a grounded grid structure. The emerging ions from the grid structure are the extracted ions. The extraction aperture can be a single grid system made of 304 stainless steel, with a mesh size of 20, and a wire width of approximately 0.014 inches.

The diameter of the flat extraction aperture is approximately 2 inches. Extracted ion energy, however, deviates significantly from the plasma energy. For ion source 16, the extraction ion energy is about 340 eV, for a plasma potential of about 550 volts. This variation is in part due to the dependence of the extracted ion energy on the physical geometry of the extraction grid and the anode ring, since this geometry dictates the shape of the equal potential planes outside ion source 16. The ion beam flux for the densification of metal oxides is approximately 5.4×10^{14} molecules/cm^2 second, as shown in Figures 5 and 6.

Neutralizer 30 provides ion beam neutralization. This is also referred to as space/charge neutralization. In space/charge neutralization, free electrons are allowed to mix with molecular ions without being captured by the electronic shell of the ions. Thus, the injection of free electrons into the ion beam produces a beam of flowing plasma.

A schematic of neutralizer 30 is shown in Figure 10. A suitable neutralizer 30 is a filamentless plasma bridge neutralizer ("FPBN") available from Nordiko, Ltd. The operational principle of neutralizer 30 is very similar to that of ion source 16. A neutral gas, including but not limited to, argon, is injected and ionized by a strong electric field. The major difference in operation principles between neutralizer 30 and ion source 16 is in voltage polarity. Because the function of neutralizer 30 is to generate and emit electrons, the inner high voltage electrode is biased negatively, typically about 500 volts, with respect to ground while the outer electrode, in this case the plasma containment housing, is biased less negatively, approximately 24 volts, with respect to ground. The inner high negative voltage is controlled via a current limited mode of about 350 mA. Therefore, electrons of the argon plasma accelerate

from a low to a high voltage gradient because the plasma potential is less than zero (negative value). The accelerated electrons then exit neutralizer 30 and mix with the positive ion beam from ion source 16. This mixing of the electrons and ions, or space-charge neutralization, is further facilitated by the fact that the extracted ion beam has a positive plasma potential. The formation of this positive potential just outside, e.g., adjacent to, neutralizer 30 creates a potential gradient with respect to the negative plasma potential inside neutralizer 30. Electrons therefore accelerate through this potential gradient.

Referring now to Figures 11 and 12, neutralizer 30 is shown in greater detail. As illustrated in Figure 11, neutralizer includes a neutralizer can, 32. Also included are the following: (i) high voltage electrode connection 34, (ii) gas inlet 36, (iii) front extraction plate 38, and (iv) an extraction aperture 40.

Referring now to Figure 12, the physical positioning of neutralizer 30 and ion source 16 is illustrated. Neutralizer 30 includes an electron beam axis which intersects an ion beam axis where there is a high positive charge. Essentially, electrons are drawn to neutralize the high positive charge. Electron beam axis can vary from 15 to approximately 20 degrees off electron beam axis, which is substantially perpendicular to neutralizer 30.

Referring now to Figure 13, vacuum chamber can be a model no. 7110 vacuum chamber commercially available from Balzars. It is equipped with a Leybold dry vac 100 beam mechanical pump and a 10 inch Balzars cryopump. The pumping speed of the system at high vacuum is about 2300 liters/second (for oxygen gas at 26 degrees centigrade, and FC flow of 15 sccm, chamber pressure of 8.0 x $10e_{-5}$ torr GP). As electron beam gun 14 outgasses, the vacuum is pulled within vacuum chamber 10. Then oxygen and argon are introduced through oxygen and argon conduits, respectively. The oxygen and argon sources are at approximately 14 psi, and the oxygen introduced into vacuum chamber is at approximately 7.0 x 10^{-5} tor. With argon beam at 4.0 x 10_{-5} tor.

Coating process procedures and parameters used in the method of the present invention are as follows:

SUBSTRATE CLEANING PROCESS

The sequence of the cleaning procedure is:

(i) hand wash and microsoap, plus deionized water solution using cotton pads;

(ii) soak in ultrasonic bath consisting of microsoap and deionized water for 10 minutes;

(iii) soak in cascaded deionized water baths (3 levels) for 10 minutes at each level; and

(iv) spin dry.

TARGET MATERIAL PLUG PREPARATION

(i) Raw material in the form of metal oxide is baked or heated using electron beam gun 14. The heating of the material continues until a molten pool forms on the target surface and plug outgassing is reduced. This typically requires an emission current of about 0.4 to 0.6 amperes at 7kV acceleration voltage. Plug outgassing is measured by observing the increase in the chamber pressure at evaporation emission current. The outgassing level is deemed acceptable when vacuum chamber 10 has a pressure change before and during evaporation that is less than about 15 percent. This type of monitoring for outgassing is made possible through manual oxygen gas feed, where total chamber pressure is not held constant via a feedback loop.

(ii) Step 1 is repeated, after raw material replenishment, until the target plug is fully formed to fill an entire 15cc crucible pocket.

ION PRECLEANING OF UNCOATED SUBSTRATES

Reactive ion precleaning or etching of uncoated substrates is accomplished just prior to the start of the coating deposition. With substrates loaded in carrier 20 in a high vacuum, reactive ion precleaning with oxygen is performed using ion source 16 and neutralizer 30. Reactive oxygen ion precleaning is effective over a large range of ion impingement angles, since the process relies on chemical interactions rather than on a physical process. This

reactive process is especially effective in removing complex hydrocarbon contaminations from the substrate surface. In a reactive oxygen environment, hydrogen layers are fragmented, yielding volatile species such as CO_2. The following are the process parameters for ion precleaning:

(i) Ion source 16 current: 400mA;

(ii) Neutralizer 30 cathode current: 350mA;

(iii) Oxygen partial pressure: 7.0×10^{-5} torr GP for ion source 16;

(iv) Argon partial pressure: 4.0×10^{-5} torr GP for neutralizer 30;

(v) Relative chamber temperature: 200 degrees centigrade;

(vi) Cleaning duration: 1 minute.

COATING PROCESS PARAMETERS

Prior to the start of coating deposition, ion source 16 and neutralizer 30 are activated to preset parameters. In order to achieve preset voltage and current values, it is first necessary to establish the flow of process gasses. This is required since gas flow, for a current limited operation, controls anode for ion source 16, and cathode for neutralizer 30, voltages. The coating deposition process parameters are as follows:

(i) Coating temperature: 200 degrees centigrade;

(ii) Oxygen partial pressure: 7.0×10^{-5} torr GP;

(iii) Argon partial pressure: 4.0×10^{-5} torr GP;

(iv) Ion source drive current: 400mA;

(v) Neutralizer 30 cathode current: 350mA.

REFRACTIVE INDEX RESULTS FOR SELECTED COATINGS

The refractive index obtained for various coatings is as follows:

(i) SiO_2 at 500nm;

(ii) Refractive index: 1.46;

Under refractive index deposition rate: 2.3 angstroms/second (6min/qwot);

(iii) HfO_2 at 500nm: Refractive index: 2.10;

Under refractive index deposition rate: 0.5 angstroms/second (18min/qwot);

(iv) Ta_2O_5 at 500nm: Refractive index: 2.15;
Deposition Rate: 0.5 angstroms/sec (18min/qwot);

(v) ZrO_2 at 500nm: Refractive Index: 2.20;
Deposition Rate: 0.5 angstroms/sec (18min/qwot);

(vi) TiO_2 at 500nm: Refractive Index: 2.65;
Deposition Rate: 0.3 angstroms/sec (25min/qwot).

The foregoing description of a preferred embodiment of the invention has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise forms disclosed. Obviously, many modifications and variations will be apparent to practitioners skilled in this art. It is intended that the scope of the invention be defined by the following claims and their equivalents.

What is claimed is:

CLAIMS

1. A method for creating a dielectric coating on a substrate, comprising:

providing a high vacuum chamber including a substrate carrier device, an electron beam gun, a substrate, an evaporant source of coating material and an ion gun;

evaporating coating material with the electron beam gun to form a coating material evaporant that is directed to the substrate;

directing the ion gun toward the substrate and producing ions that arrive substantially simultaneously with the coating material evaporant at the substrate, the ions providing a momentum assist to the coating material evaporant; and

forming a dielectric thin film of coating material on the substrate.

2. The method for creating a dielectric coating on a substrate of claim 1, wherein a plasma beam neutralizer is provided.

3. The method for creating a dielectric coating on a substrate of claim 1, wherein the dielectric coating is an optical coating.

4. The method for creating a dielectric coating on a substrate of claim 1, wherein a plurality of dielectric thin films of coating material are formed on the substrate.

5. The method for creating a dielectric coating on a substrate of claim 1, further comprising:

controlling the stoichiometry of the coating material layers formed on the substrate.

6. The method for creating a dielectric coating on a substrate of claim 1, further comprising:

controlling an ion/coating material evaporant arrival ratio at the substrate to created a desired density of coating material dielectric thin film layers.

7. The method for creating a dielectric coating on a substrate of claim 1, wherein the ions increase the energy of the coating material deposited as layers on the substrate.

8. The method for creating a dielectric coating on a substrate of claim 7, wherein the energy of the coating material deposited as layers on the substrate is greater than 5 eV.

9. The method for creating a dielectric coating on a substrate of claim 7, wherein the energy of the coating material deposited as layers on the substrate is greater than 7.5 eV.

10. The method for creating a dielectric coating on a substrate of claim 7, wherein the energy of the coating material deposited as layers on the substrate is greater than 9.0 eV.

11. The method for creating a dielectric coating on a substrate of claim 7, wherein the energy of the coating material deposited as layers on the substrate is 10.0 eV or greater.

12. The method for creating a dielectric coating on a substrate of claim 1, wherein the dielectric coating has a low scatter of less than 50 ppm.

13. The method for creating a dielectric coating on a substrate of claim 1, wherein the dielectric coating has a low loss of less than about 100 ppm.

14. The method for creating a dielectric coating on a substrate of claim 1, wherein the dielectric coating has an environmental stability of 0.1% spectral shift or less.

15. The method for creating a dielectric coating on a substrate of claim 1, wherein the ion gun produces positively charged particles along a longitudinal axis of the ion gun at the exterior of the ion gun.

16. The method for creating a dielectric coating on a substrate of claim 15, wherein the neutralizer produces electrons which mix with the positively charged particles along the longitudinal axis of the ion gun at the exterior of the ion gun, producing a beam of flowing plasma.

17. The method for creating a dielectric coating on a substrate of claim 1, wherein the neutralizer is a filamentless plasma bridge neutralizer.

18. The method for creating a dielectric coating on a substrate of claim 1, wherein the ion source is a cold cathode ion source.

19. The method for creating a dielectric coating on a substrate of claim 1, wherein the coating material is a metal oxide.

20. The method for creating a dielectric coating on a substrate of claim 1, wherein the metal oxide is selected from the group, SiO_2, HfO_2, Ta_2O_5, ZrO_2, TiO_2, Nb_2O_5, Y_2O_3, Al_2O_3, Se_2O_3, BeO and Gd_2O.

21. The method for creating a dielectric coating on a substrate of claim 1, wherein the coating material is a metal fluoride.

22. The method for creating a dielectric coating on a substrate of claim 1, wherein the coating material is a metal carbide.

23. The method for creating a dielectric coating on a substrate of claim 1, wherein the coating material is a metal nitride.

24. A method for creating a dielectric coating on a substrate, comprising:

providing a high vacuum chamber including a substrate carrier device, an electron beam gun, a substrate, an evaporant source of coating material, a plasma beam neutralizer and an ion gun producing positively charged particles along a longitudinal axis of the ion gun;

positioning the plasma beam neutralizer adjacent to and in a lateral direction relative to the ion gun longitudinal axis;

generating electrons from the plasma beam neutralizer which mix with the positively charged particles along the longitudinal axis of the ion gun at the exterior of the ion gun, producing a beam of flowing plasma;

evaporating coating material with the electron beam gun to form a coating material evaporant that is directed to the substrate;

providing a momentum assist from the beam of flowing plasma to the coating material evaporant; and

forming a dielectric thin film of coating material on the substrate.

25. The method for creating a dielectric coating on a substrate of claim 24, wherein the dielectric coating is an optical coating.

26. The method for creating a dielectric coating on a substrate of claim 24, wherein a plurality of dielectric thin films of coating material is formed on the substrate.

27. The method for creating a dielectric coating on a substrate of claim 24, further comprising:

controlling the stoichiometry of the coating material layers formed on the substrate.

28. The method for creating a dielectric coating on a substrate of claim 24, further comprising:

controlling a plasma/coating material evaporant arrival ratio at the substrate to created a desired density of coating material dielectric thin film layers.

29. The method for creating a dielectric coating on a substrate of claim 24, wherein the plasma increases the energy of the coating material deposited as layers on the substrate.

30. The method for creating a dielectric coating on a substrate of claim 24, wherein the energy of the coating material deposited as layers on the substrate is greater than 5 eV.

31. The method for creating a dielectric coating on a substrate of claim 24, wherein the energy of the coating material deposited as layers on the substrate is greater than 7.5 eV.

32. The method for creating a dielectric coating on a substrate of claim 24, wherein the energy of the coating material deposited as layers on the substrate is greater than 9.0 eV.

33. The method for creating a dielectric coating on a substrate of claim 24, wherein the energy of the coating material deposited as layers on the substrate is 10.0 eV or greater.

34. The method for creating a dielectric coating on a substrate of claim 24, wherein the dielectric coating has a low scatter of less than 50 ppm.

35. The method for creating a dielectric coating on a substrate of claim 24, wherein the dielectric coating has a low loss of less than about 100 ppm.

36. The method for creating a dielectric coating on a substrate of claim 24, wherein the dielectric coating has an environmental stability of 0.1% spectral shift or less.

37. The method for creating a dielectric coating on a substrate of claim 24, wherein the ion gun produces positively charged particles along a longitudinal axis of the ion gun at the exterior of the ion gun.

38. The method for creating a dielectric coating on a substrate of claim 24, wherein the neutralizer is a filamentless plasma bridge neutralizer.

39. The method for creating a dielectric coating on a substrate of claim 24, wherein the ion source is a cold cathode ion source.

40. The method for creating a dielectric coating on a substrate of claim 24, wherein the coating material is a metal oxide.

41. The method for creating a dielectric coating on a substrate of claim 24, wherein the metal oxide is selected from the group, SiO_2, HfO_2, Ta_2O_5, ZrO_2, TiO_2, SiO_2, HfO_2, Ta_2O_5, ZrO_2, TiO_2, Nb_2O_5, Y_2O_3, Al_2O_3, Se_2O_3, BeO and Gd_2O.

42. The method for creating a dielectric coating on a substrate of claim 24, wherein the coating material is a metal fluoride.

43. The method for creating a dielectric coating on a substrate of claim 24, wherein the coating material is a metal carbide.

44. The method for creating a dielectric coating on a substrate of claim 24, wherein the coating material is a metal nitride.

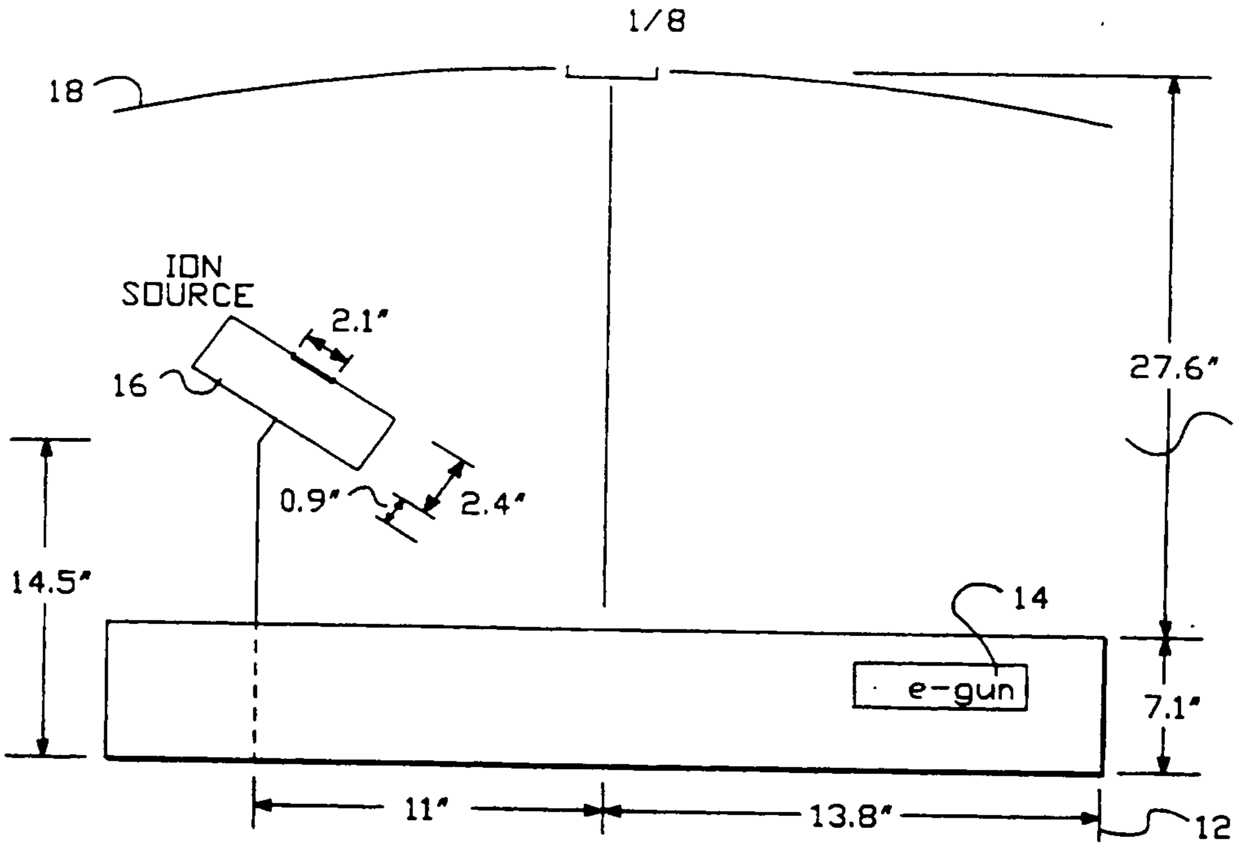

FIG. 1

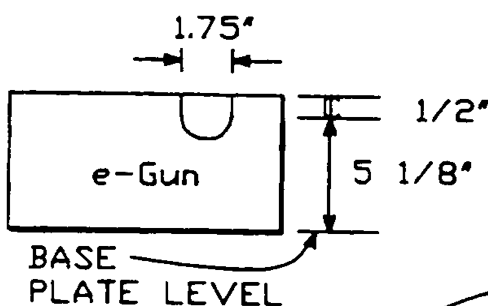

FIG. 2

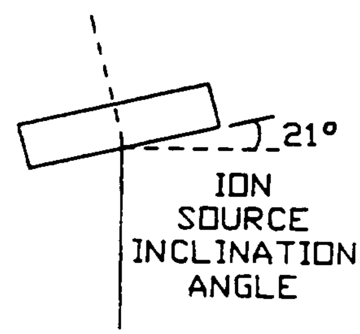

FIG. 3

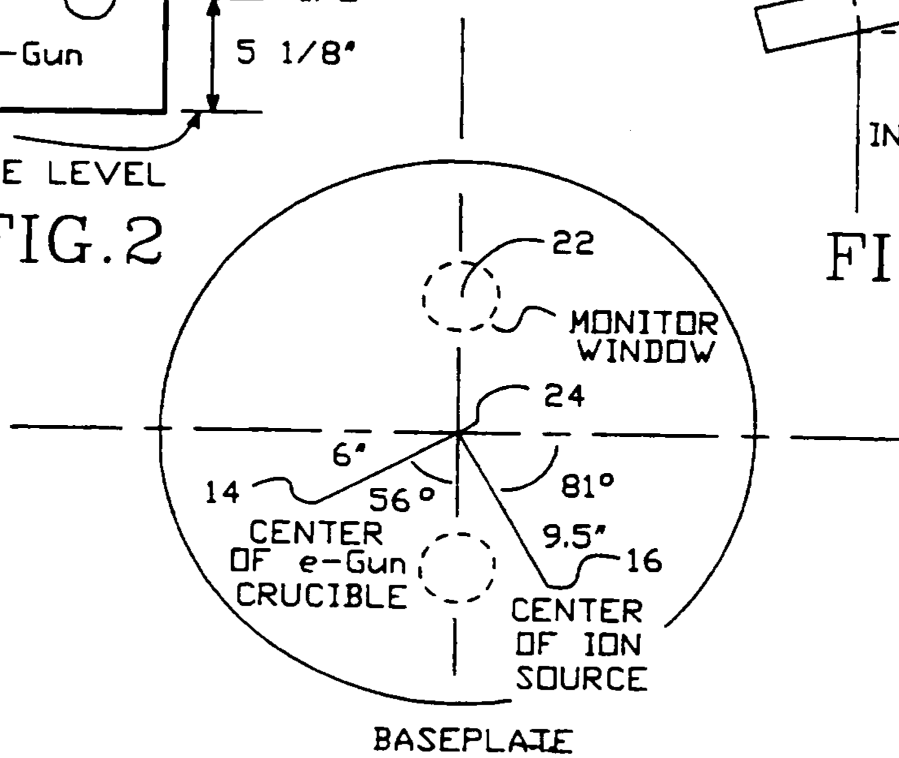

FIG. 4

REFRACTIVE INDEX AS A FUNCTION OF DEPOSITION RATE :

- $Ta_2 O_5$ -

RATE @ 550 nm	EVAPORANT FLUX	ION FLUX	EVAP : ION RATIO	REFRACTIVE INDEX
3 MIN.	4.4×10^{14} MOLEC./S.cm^2	NO IONS	N/A	2.05
10 MIN.	1.3×10^{14} MOLEC./S.cm^2	5.4×10^{14} MOLEC./S.cm^2	1 : 4.2	2.12
25 MIN.	4.9×10^{13} MOLEC./S.cm^2	•	1 : 1.1	2.20

FIG.5

- TiO_2 -

RATE @ 550 nm	EVAPORANT FLUX	ION FLUX	EVAP : ION RATIO	REFRACTIVE INDEX
5 MIN.	5.7×10^{14} MOLEC./S.cm^2	5.4×10^{14} MOLEC./S.cm^2	~ 1 : 1	2.50
9 MIN.	3.2×10^{14} MOLEC./S.cm^2	•	1 : 1.7	2.57
25 MIN.	1.1×10^{14} MOLEC./S.cm^2	•	1 : 4.9	2.65

COATING TEMPERATURE : 200° C
ION SPECIES : OXYGEN
ION ENERGY : ~ 550 eV (PLASMA ENERGY INSIDE ION SOURCE)

FIG.6

Ion Source Schematic Diagram

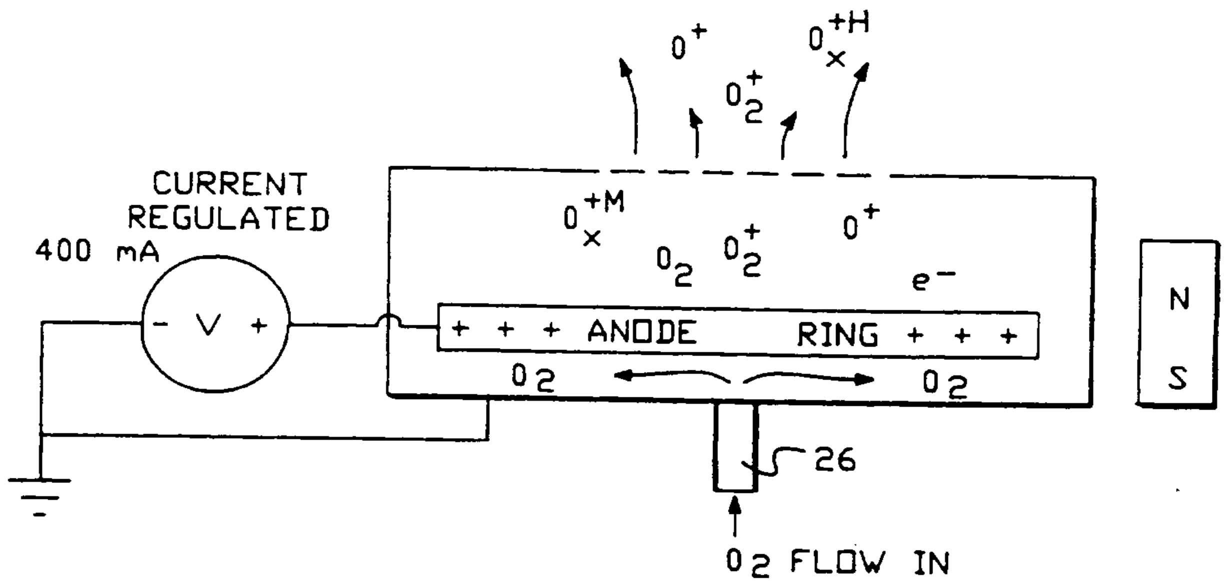

FIG.7

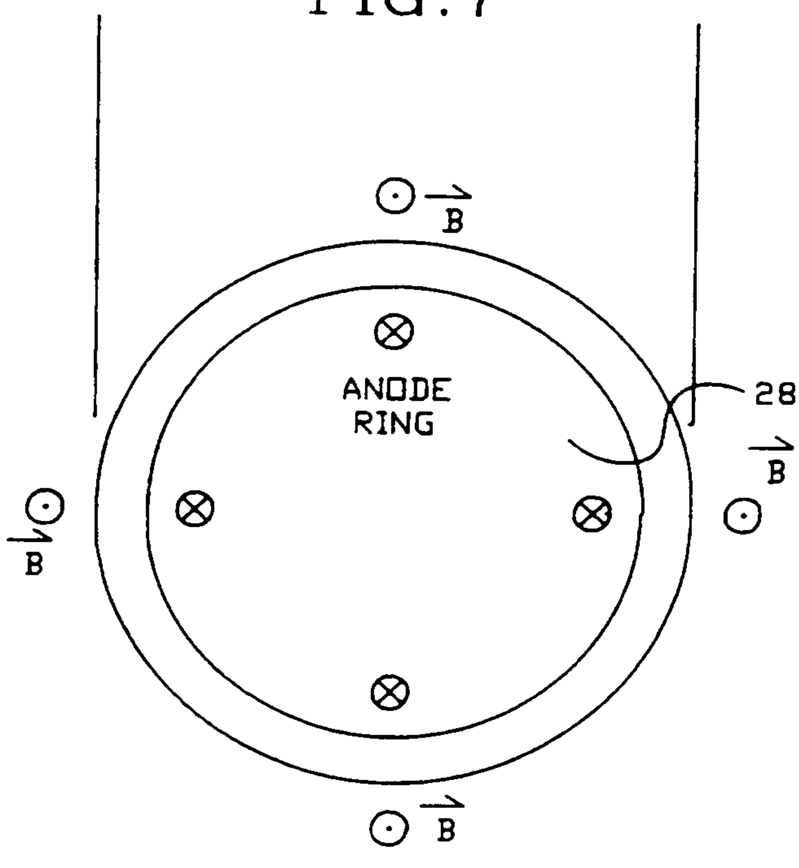

FIG.8

SUBSTITUTE SHEET (RULE 26)

Ion Source & Neutralizer Schematic Diagram

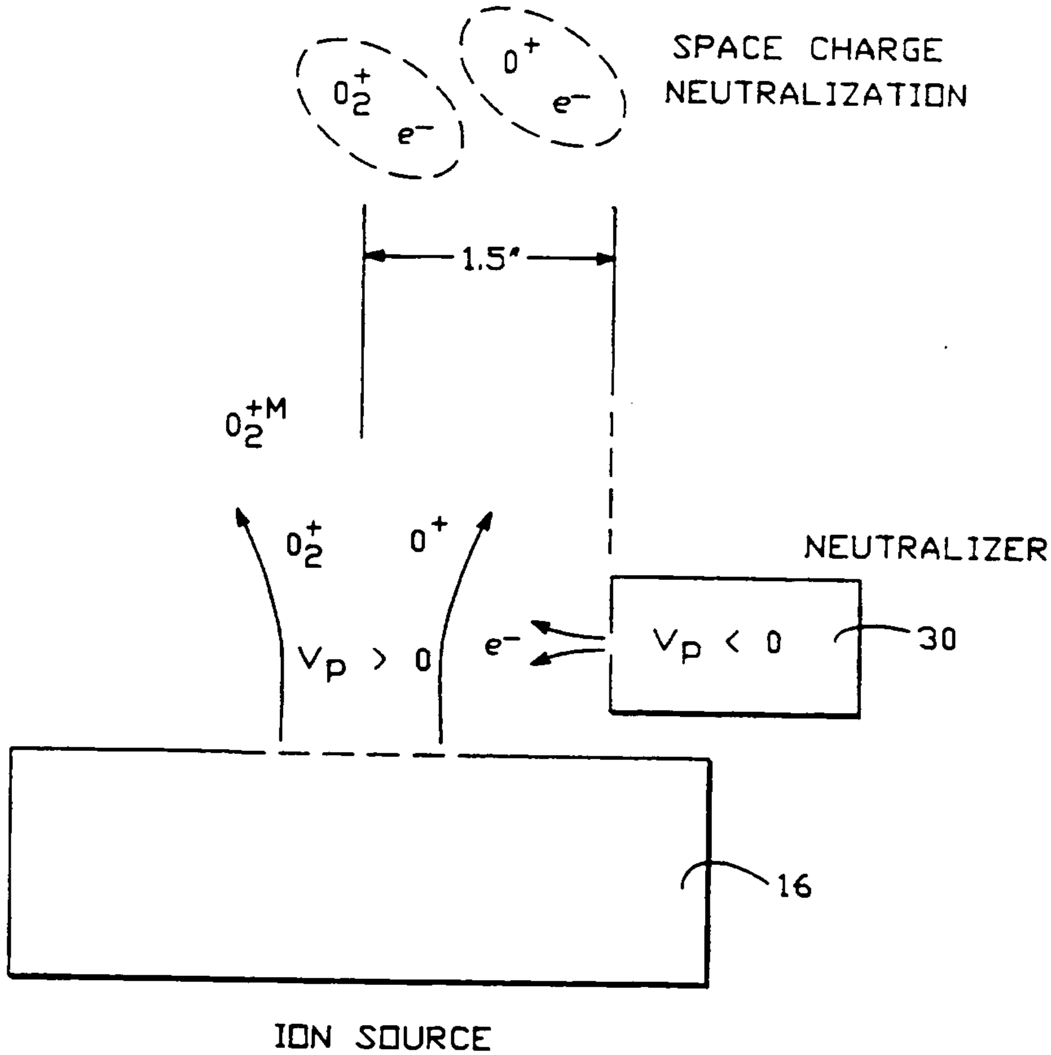

FIG.9

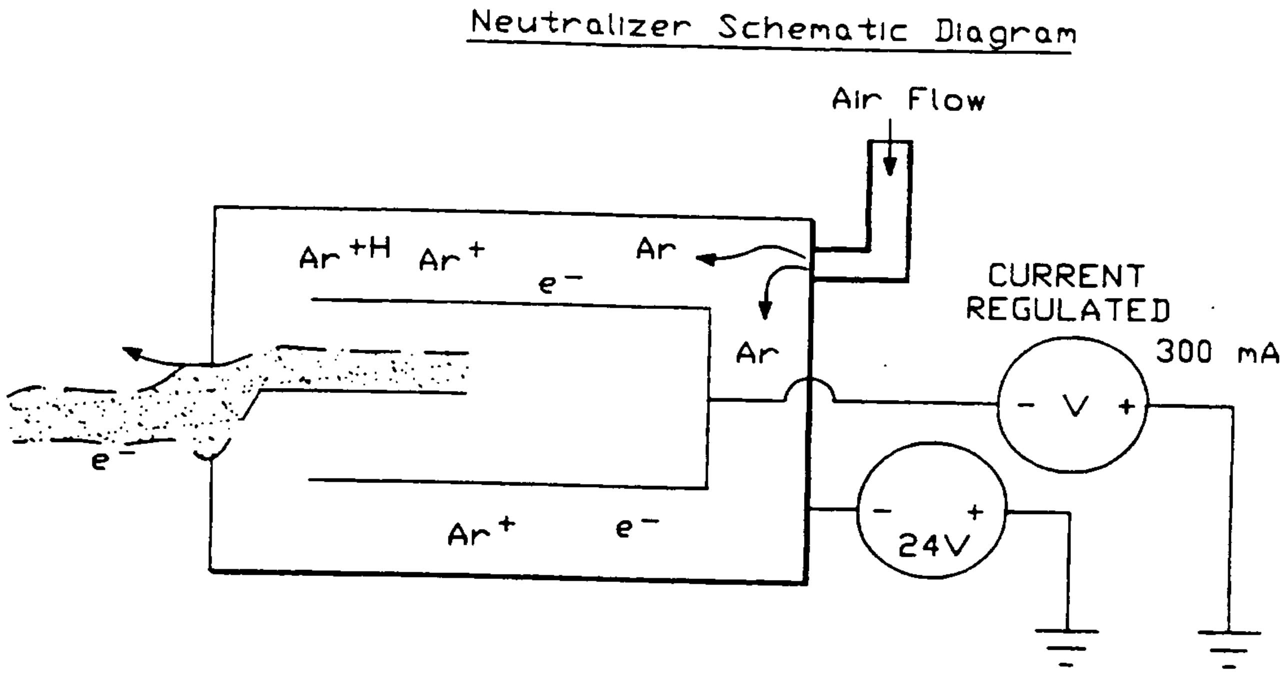
Neutralizer Schematic Diagram
Air Flow
Ar +H Ar +
e −
Ar
Ar
e −
Ar +
e −
CURRENT
REGULATED
300 mA
− V +
− +
24V

FIG.10

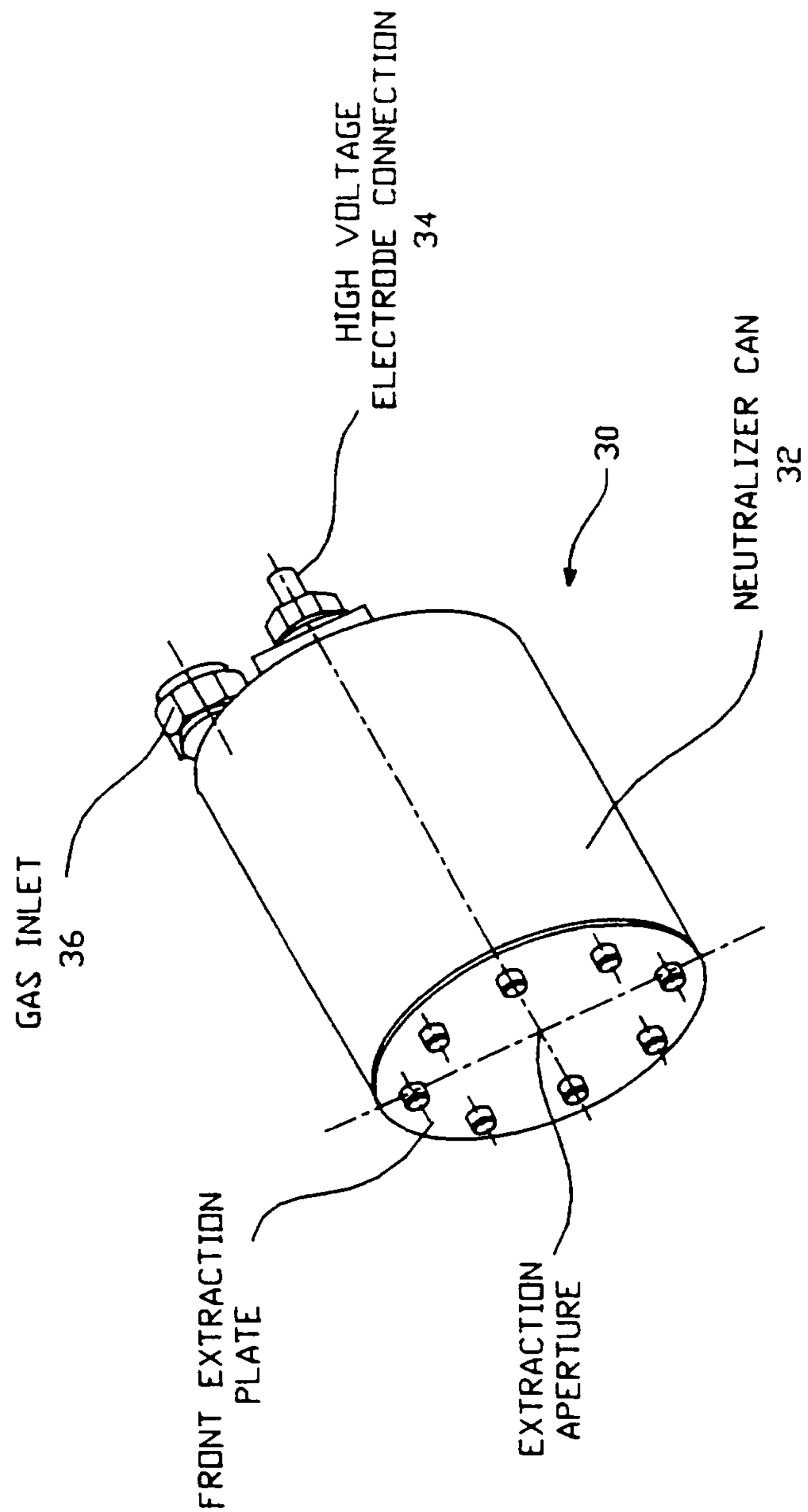
HIGH VOLTAGE
ELECTRODE CONNECTION
34
30
NEUTRALIZER CAN
32
GAS INLET
36
FRONT EXTRACTION
PLATE
EXTRACTION
APERTURE

FIG.11

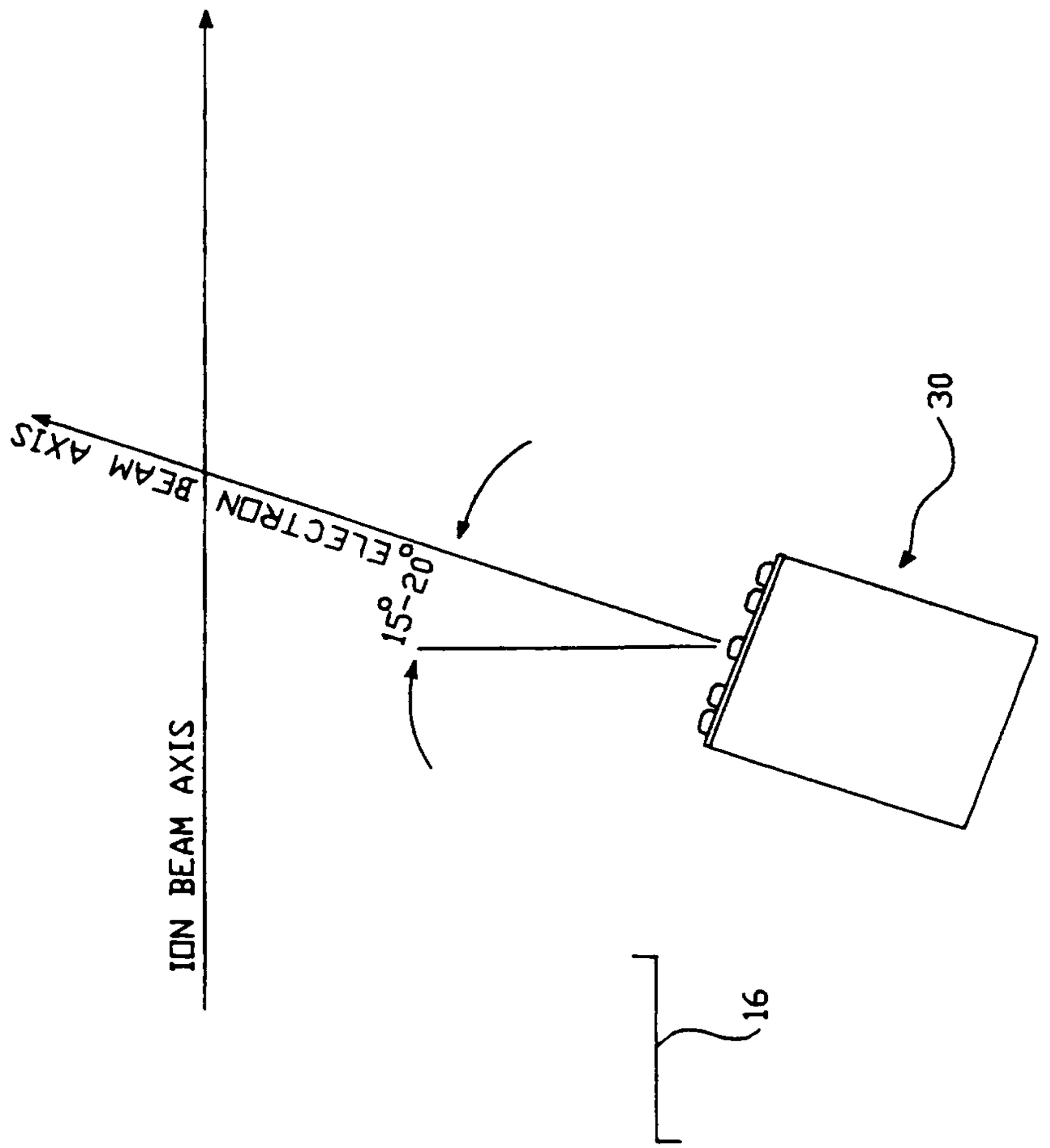

FIG. 12

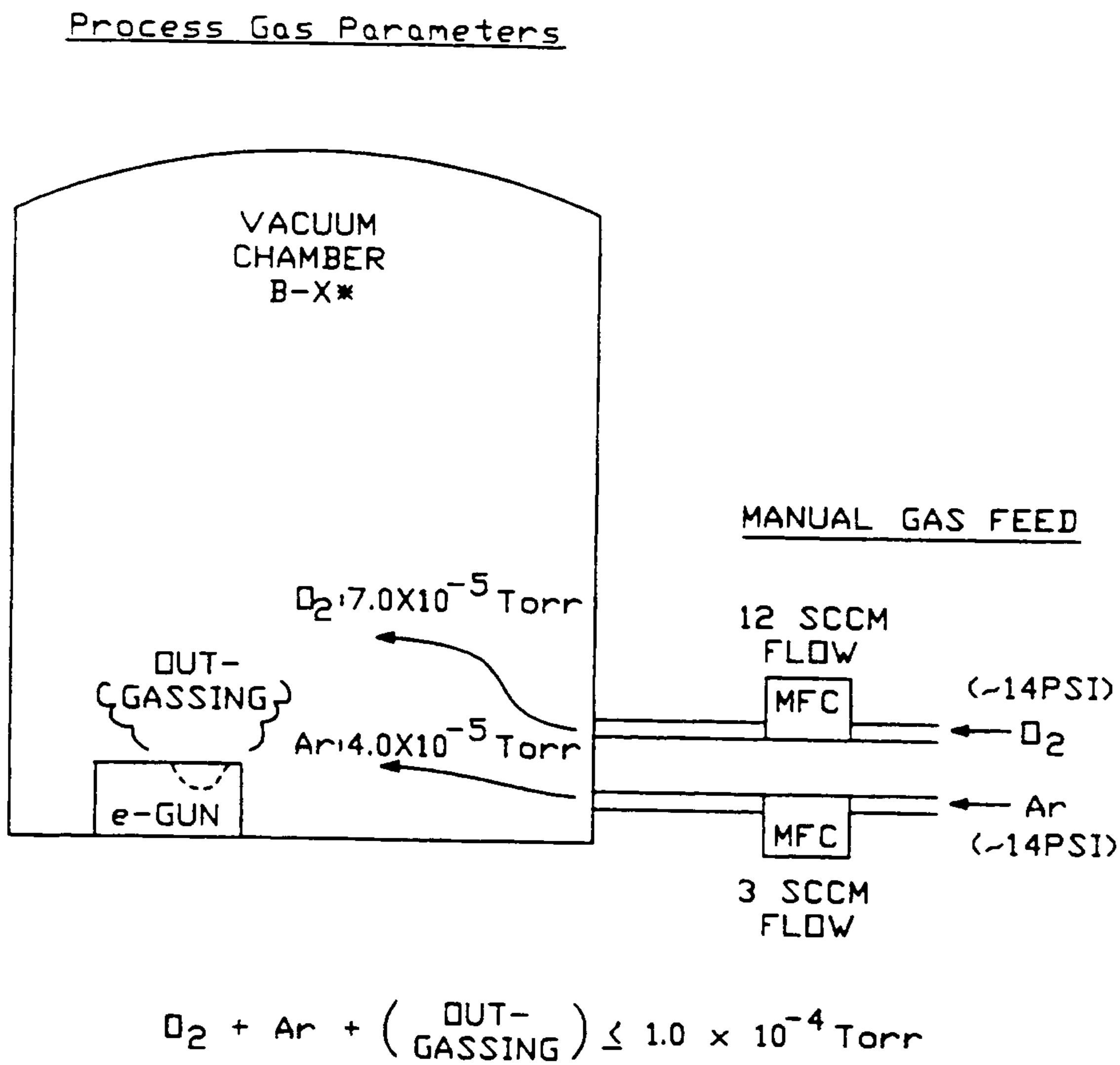
Process Gas Parameters
VACUUM CHAMBER B-X*
MANUAL GAS FEED
O_2: 7.0×10^{-5} Torr
12 SCCM FLOW
OUT-GASSING
MFC
(~14PSI)
O_2
Ar: 4.0×10^{-5} Torr
e-GUN
Ar
MFC
(~14PSI)
3 SCCM FLOW
O_2 + Ar + (OUT-GASSING) $\leq 1.0 \times 10^{-4}$ Torr

FIG. 13

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/05101

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C23C14/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB,A,2 194 555 (NIPPON TELEGRAPH & TELEPHONE) 9 March 1988	1-3,5-7, 15,19, 24,25, 27-29, 37,40
Y	see page 1, line 44 - line 49	16,17, 21,38,42
	see page 2, line 53 - page 3, line 17	

X	US,A,5 179 318 (MAEDA MICHIHISA ET AL) 12 January 1993 see column 11, line 57 - column 12, line 21	1,3,4, 15,18-20

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

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Date of the actual completion of the international search	Date of mailing of the international search report
30 July 1996	08.08.96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Ekhult, H

International Application No
PCT/US 96/05101

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	35TH NATIONAL SYMPOSIUM OF THE AMERICAN VACUUM SOCIETY, ATLANTA, GA, USA, 2-7 OCT. 1988, vol. 7, no. 3, pt.2, ISSN 0734-2101, JOURNAL OF VACUUM SCIENCE & TECHNOLOGY A (VACUUM, SURFACES, AND FILMS), MAY-JUNE 1989, USA, pages 2286-2288, XP000133796 WILLIAMS F L ET AL: "Metal oxides deposited using ion assisted deposition at low temperature" see page 2278, left-hand column, line 26 - line 30 ---	1,3,5,6, 12
X	US,A,5 015 353 (HUBLER GRAHAM K ET AL) 14 May 1991 see claim 1 ---	1,3,5,23
X	APPLIED PHYSICS LETTERS, 21 MARCH 1994, USA, vol. 64, no. 12, ISSN 0003-6951, pages 1514-1516, XP000434335 MING LU ET AL: "Growth of cubic boron nitride on Si(100) by neutralized nitrogen ion bombardment"	1,23
A	see page 1514, right-hand column, line 16 - page 1515, left-hand column, line 10 ---	44
Y	PROCEEDINGS OF THE 14TH SYMPOSIUM ON ELECTRON, ION AND PHOTON BEAM TECHNOLOGY, PALO ALTO, CA, USA, 25-27 MAY 1977, vol. 15, no. 3, ISSN 0022-5355, JOURNAL OF VACUUM SCIENCE AND TECHNOLOGY, MAY-JUNE 1978, USA, pages 1093-1095, XP000576457 READER P D ET AL: "Argon plasma bridge neutralizer operation with a 10-cm-beam-diameter ion etching source" see abstract; figure 1 ---	17,38
Y	PATENT ABSTRACTS OF JAPAN vol. 015, no. 512 (C-0898), 26 December 1991 & JP,A,03 226555 (OLYMPUS OPTICAL CO LTD), 7 October 1991, see abstract ---	21,42
Y	PATENT ABSTRACTS OF JAPAN vol. 007, no. 084 (E-169), 7 April 1983 & JP,A,58 012317 (SONY KK), 24 January 1983, see abstract ---	16

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	APPLIED OPTICS, 1 JAN. 1983, USA, vol. 22, no. 1, ISSN 0003-6935, pages 178-184, XP002009629 MARTIN P J ET AL: "Ion-beam-assisted deposition of thin films" see figure 9 ---	14,36
A	APPLIED OPTICS, 15 SEPT. 1984, USA, vol. 23, no. 18, ISSN 0003-6935, pages 3047-3049, XP000575296 WINDT D L ET AL: "Ion beam deposited silicon carbide on glass optics and replica gratings" see page 3047, column ER, line 9 - line 26 ---	22,43
A	PROCEEDINGS OF THE 3RD INTERNATIONAL CONFERENCE ON LOW ENERGY ION BEAMS, LOUGHBOROUGH, UK, 28-31 MARCH 1983, vol. 34, no. 1-2, ISSN 0042-207X, VACUUM, JAN.-FEB. 1984, UK, pages 291-294, XP000576321 HOWSON R P ET AL: "Reactive ion plating of TiO/sub 2/" see figure 1 -----	1-44

1

INTERNATIONAL SEARCH REPORT

...ormation on patent family members

Intern... al Application No
PCT/US 96/05101

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A-2194555	09-03-88	JP-A- 63035493	16-02-88
		JP-B- 7053634	07-06-95
		JP-A- 63107892	12-05-88
		FR-A- 2602246	05-02-88
		US-A- 4888202	19-12-89
		US-A- 5016563	21-05-91
US-A-5179318	12-01-93	JP-A- 3241642	28-10-91
		JP-A- 3196448	27-08-91
		GB-A,B 2237141	24-04-91
		NL-A- 9001542	01-02-91
		JP-A- 3156838	04-07-91
US-A-5015353	14-05-91	NONE	